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Effect of sulfur in catalytic partial oxidation of methane over Rh–Ce coated foam monoliths

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Abstract

A potentially important technology to convert natural gas to syngas is catalytic partial oxidation (CPO) over precious metal catalysts. However, natural gas contains small amounts of sulfur compounds which can poison the catalyst. It is therefore of interest to investigate the effect of sulfur on the performance of CPO. In this work CPO experiments have been performed over Rh–Ce coated foam monoliths with CH_3SH added to methane. The result of ppm levels of sulfur is a large ($\sim 200\,^{\circ}C$) temperature increase, along with lower methane conversion and lower hydrogen selectivity. A doubling of the sulfur level from 14 to 28 ppm does not result in significant changes, showing that the effect saturates at a few ppm. The poisoning effect has been investigated by analyzing both effluent and spatially resolved data and is shown to be due to severe hindrance of steam reforming by adsorbed sulfur.
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1. Introduction

In order to utilize a larger part of world's natural gas resources it is of interest to convert natural gas to liquid fuels. Liquid fuels are easier to transport from remote and small fields where economics prohibit building a gas pipeline [1]. The current proven reserves to current production ratio is 50% higher for natural gas than oil [2], and this offers the potential for partly offsetting the predicted decline in oil production.

Since natural gas, mostly methane, is difficult to convert directly to liquid fuels, the preferred route is first to produce syngas, and then convert this to methanol or to higher alkanes by Fischer–Tropsch synthesis [2]. It is therefore of interest to study the production of syngas from methane. The work by Hickman and Schmidt showed that catalytic partial oxidation (CPO) of methane (Eq. (1)) on foam monoliths with precious metal catalyst is an attractive way to obtain syngas [3]. One advantage is that the process is slighty exothermic, whereas steam reforming (SR) (Eq. (2)) is endothermic.

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2, \qquad \Delta H_r^{\circ} = -36\,\mathrm{kJ\,mol^{-1}}, \tag{1}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2, \qquad \Delta H_r^{\circ} = +206\,\mathrm{kJ\,mol^{-1}}. \tag{2}$$

The kinetics of SR is substantially slower than that of CPO which allows for more compact systems. This in turn makes the systems interesting for remote gas fields. An additional advantage of CPO is that it produces a H_2/CO-ratio of 2, which is needed for the downstream processing to liquid fuels [4].

The mechanism for CPO has been subject of much debate in the literature and was recently reviewed [5]. The debate has focused on whether the reaction follows a path of combustion followed by reforming ('indirect path') or hydrogen is formed directly ('direct path'). Part of the debate is due to the wide variety of conditions that have been used in the different experiments yielding different results. However, the current understanding leans towards a more complex view than either of the simple models suggest [6].

One of the challenges for the CPO process is the presence of sulfur compounds in natural gas in the form of, e.g. mercaptans and H_2S. It is well known that sulfur acts as a poison for many catalyst, and it has been shown to be the case for CPO of higher alkanes such as tetradecane [7]. Recently the effect of high

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levels of thiophene (7400 ppm) on CPO of methane over $NiCoMgCeO_x$ catalyst supported on zirconia–haffnia was reported. Thiophene was shown to decrease the conversion of both CH_4 and O_2 and the selectivity to H_2 and CO decreased from from 99 to 5% and 98 to 45% over 6 h, respectively. It was furthermore shown that complete regeneration was possible by passing an O_2/N_2 mixture over the catalyst [8]. To our knowledge the only other studies of the effect of sulfur on CH_4 conversion where conducted under combustion conditions [9,10]. Both studies found that sulfur deactivates the catalyst which was ascribed to the formation of sulfates.

This work investigates the effect of sulfur on Rh–Ce catalysts on alumina foam monoliths under different feed stochiometries (carbon to oxygen (C/O) ratios) and the effect of steam addition. Furthermore, spatial profiles of the gaseous species and surface and gas temperature through the monolith have been measured. These profiles show how the products and reactants evolve through the monolith which allows us to separate the dominant reactions such as total oxidation, steam reforming, and water-gas-shift (WGS). Finally a comparison of catalysts sulfur tolerance between Rh–Ce and Pt will be presented.

2. Experimental

Reactant gases CH_4, O_2, N_2 and CH_3SH/N_2 (1/99 vol.) were introduced through calibrated mass flow controllers. Steam was introduced by feeding water from a syringe pump through a furnace before mixing it with the permanent gases. The reported sulfur level (0, 14, and 28 ppm) is mole percent based on the total flow of gases. The level of sulfur is higher than what is allowed in pipeline quality gas (8 ppm [11] or equivalent of ~ 2 ppm based on total flows and concentrations in the current work). The reported data should therefore be taken as a worst case scenario. The chosen level was dictated by the lower limit of the mass flow controllers that would allow accurate delivery to the system. In the spatial profile measurements Ar replaced N_2 in order to avoid overlaps at mass 28 in the quadropole mass spectrometer (QMS).

Catalysts were prepared using the incipient wetness technique using 5 mm long 17 mm diameter 80 ppi α-alumina foam monoliths as described else where [12]. The washcoat was applied as γ-alumina with a loading of 3 wt.% of the monolith and calcined for 6 h at 600 °C. Subsequently $Rh(NO_3)_3$ and $Ce(NO_3)_3$ were co-precipitated with a nominal loading of 0.5 and 2 wt.%, respectively. The addition of Ce helps stabilize the surface area of the washcoat [13] and thus maintain a higher activity of the catalyst. Pt catalysts were prepared from H_2PtCl_6 solution with a metal loading of 0.5 wt.% After the metal was precipitated the catalyst was calcined at 600 °C in air for 6 h for Rh–Ce and H_2 for Pt to avoid loss of volatile Pt oxides. The reactor used was a 600 mm quartz tube with an i.d. of 18 mm. The gases were fed from the top and passed through a furnace to preheat the gases to 200 °C. A blank 5 mm monolith was placed at the end of the heated section to ensure mixing. The catalyst (5 mm long 17 mm diameter monolith) was placed 70 mm downstream of the furnace between two blank 10 mm monoliths that act as heat shields. All monoliths were wrapped in ceramic paper to eliminate gas bypass. The reactor section was insulated to avoid heat losses. The reported temperature of T_{feed} was measured 60 mm upstream of the catalyst, and T_{back} is the back face temperature of the catalyst.

The CPO experiments were conducted by flowing gases at $T_{feed} = 200\,^\circ$ C at a GHSV of 7.5×10^5 h^{-1} and at $T_{feed} = 70\,^\circ$ C at a GHSV of 1.3×10^5 h^{-1} for the effluent and spatial experiments, respectively. The GHSV is defined as the volumentric flow rate (at STP 0 °C, 101 kPa) divided by the volume of the monolith.

In the case where steam was not used it was substituted by adding extra N_2 thus maintaining the GHSV. The feed compositions, defined by the carbon to oxygen ratio (C/O), are $C/O = 0.73$, 1.0 and 1.3—not counting the oxygen in steam. To ensure that the blank monoliths were not catalytic blank runs were performed which showed negligible activity. The catalyst was lit off by heating it to 50 °C in N_2 or Ar by a heat gun and then passing a mixture of $H_2/O_2/N_2$ (0.3:0.2:3 Slpm) over the catalyst. This readily lights the catalysts off and when a back face temperature of 300 °C is achieved the feed is switched to methane.

For the SR experiments the GHSV was 2×10^5 h^{-1} with a steam to carbon ratio (S/C) of 2 with a 52% mole fraction of N_2. In these experiments the feed was preheated to 950 °C. Again, blank runs were used to check for catalytic activity on the foam monoliths with negligible activity.

The effluent of the reactor was analyzed using a GC (HP6890 with Plot-Q column), and the water content was determined by closing the oxygen balance. The C- and H-balance closed in all cases with ± 3 and ±5%, respectively. It was not possible to detect any sulfur compounds in the effluent due their low concentration. However, thermodynamics predict that all sulfur will be converted to H_2S at the outlet, which is in agreement with observations on Rh-based catalysts by Fisher et al. which showed that the form of sulfur (i.e. thiophene, sulfurdioxide, benzothiophene, dibenzothiophene) introduced does not affect the poisoning of the catalyst [14]. Eqs. (3) and (4) show the definitions of selectivities and conversion, respectively, employed in this work.

$$S_{i,j} = 100\frac{\nu_i F_j^{out}}{\nu_i (F_{CH_4}^{in} - F_{CH_4}^{out})} \tag{3}$$

$$X_i = 100\frac{(F_i^{in} - F_i^{out})}{F_i^{in}} \tag{4}$$

where $S_{i,j}$ is the selectivity of component j with respect to the atomic basis i (i =C, H) in methane. ν is the stoichiometric coefficient and F is the flow rate. X_i is the conversion of component of i.

Fig. 1 shows a schematic of the system used in the spatial experiments. Spatial profiles were obtained on 10 mm long monoliths with identical washcoat and metal loadings using the capillary technique [5]. The current setup has been modified by including a stepper motor to position the capillary. This modification allows for > 500 data points to be obtained

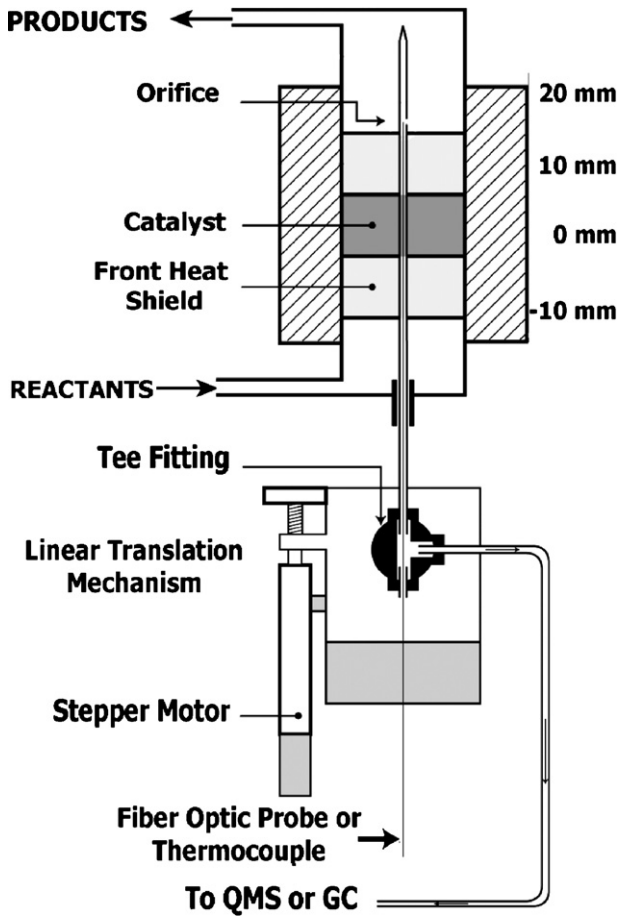

Fig. 1. Experimental setup for capillary technique.

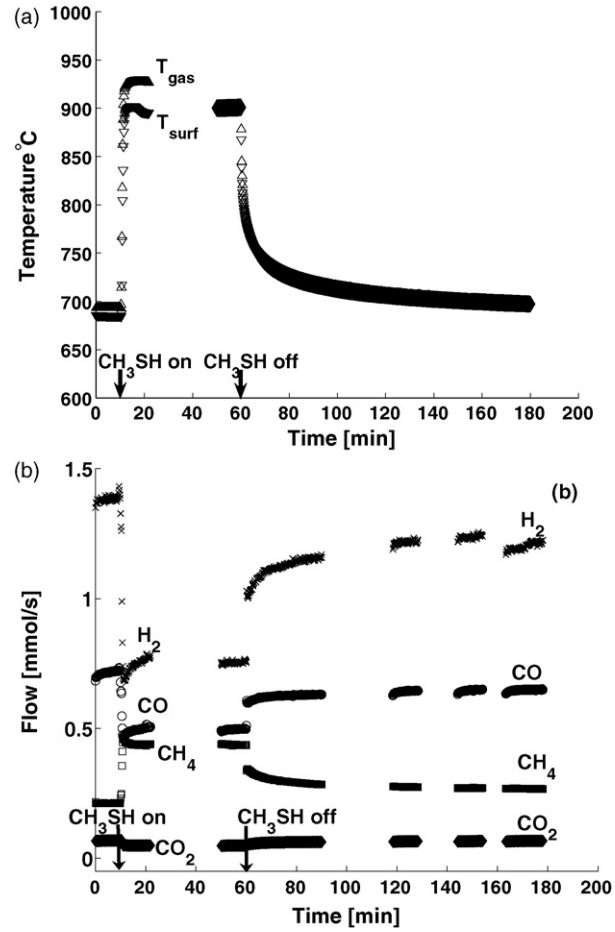

Fig. 2. Effect of CH_3SH addition (14 ppm) at the back of the catalyst on (a) temperatures, T_{surf} (▽), T_{gas} (△) and (b) the flow of CH_4 (□), CO (○), CO_2 (◇), H_2 (×), catalyst Rh(0.5%)–Ce(2%), 3% γ-Al_2O_3 on 80 ppi α-Al_2O_3. GHSV = 1.3×10^5 h^{-1} C/O = 1, S/C = 0, T_{feed} = 70 °C.

during a single run, with the resolution determined by coarseness of the monolith (∼300 μm diameter channels), since the orifice in the capillary is ∼200 μm. In addition an optical pyrometer was used to obtain surface temperature measurements by insertion of an optical fiber in the channel. Temperatures measured by insertion of thermocouple are believed to be closer to the gas temperature since the entire length is subjected to the gas flow.

The data shown in this work were repeated on at least two different catalyst. The total time on stream for each catalyst was at least 4 h and in most cases more than 30 h. Effluent data are reported as atomic selectivities and conversions given by Eqs. (3) and (4) respectively, while spatial data are reported in mmol s^{-1}.

3. Results

Fig. 2 shows the effect of adding 14 ppm CH_3SH to the feed under CPO conditions. The temperatures rise by ∼200 °C, and at the new steady state the production of H_2 has decreased by 45% from the non-sulfur level. This is accompanied by a increase in the flow of methane of 20% due to lower conversions. Furthermore, it is seen that the catalyst only recovers slowly to its original state when CH_3SH is removed from the feed. Similar results (not shown) for introduction of CH_3SH were obtained on pure Rh catalyst. It is possible to bring the catalyst back to its original state faster by reducing the catalyst in H_2 for ∼10 min at 600 °C. At C/O = 1, and 1.3 it is also possible to decrease the recovery period by decreasing the C/O-ratio for a few minutes to obtain a temperature close to what was seen during sulfur exposure before returning to the original conditions. At C/O = 0.73 the same procedure seemed to result in some loss of catalytic activity, probably due to overheating in the front face of the catalyst.

Table 1
Effect of CH_3SH addition at different C/O-ratio

	C/O = 0.73		C/O = 1.0		C/O = 1.3	
	0 ppm	28 ppm	0 ppm	28 ppm	0 ppm	28 ppm
T_{back} (°C)	799	1082	690	1013	688	933
X_{CH_4} (%)	83	54	63	36	43	25
S_{H,H_2} (%)	81	41	83	28	81	23
$S_{C,CO}$ (%)	83	79	82	76	82	76
S_{C,CO_2} (%)	13	16	13	16	17	20
S_{H,H_2O} (%)	24	63	21	73	25	80

Catalyst Rh(0.5%)–Ce(2%), 3% γ-Al_2O_3 on 80 ppi α-Al_2O_3. GHSV = 7.5×10^5 h^{-1}, S/C = 0, T_{feed} = 200 °C.

Table 1 shows the effect for the different C/O-ratios upon addition of sulfur in the feed. It is observed that the decline in S_{H,H_2} is stronger for higher C/O-ratios while $S_{C,CO}$ remains almost constant for all ratios. Furthermore the rise in temperature and the drop in hydrogen selectivity shown in Table 1 indicates that the endothermic SR is strongly affected by the presence of sulfur on the surface. The effect on SR inhibition is further supported by the change in flows between 0 and 28 ppm sulfur for H_2 to CO is close to 3 for all C/O-ratios as would be expected from Eq. (2).

Table 2 compares the effect of adding steam with a S/C-ratio = 1 with 28 ppm CH_3SH in the feed. It is seen that S_{H,H_2} is increased with steam addition and that the temperature difference with and without steam is small for all C/O.

An experiment feeding only CH_4 and steam was performed to further test sulfur's effect on SR, the results of which are shown in Table 3. The reason for the higher sulfur content in this experiment is due to the lower flow limit of the mass flow controller. It is seen that sulfur completely shuts down the SR reaction in this experiment and makes the catalyst comparable to a blank monolith.

Fig. 3 shows spatial profiles obtained using the capillary technique [5] for three different levels of sulfur (0, 14 and

Table 2
Effect of steam addition with 28 ppm CH_3SH at different C/O-ratio (Catalyst Rh(0.5%)–Ce(2%), 3% γ-Al_2O_3 on 80 ppi α-Al_2O_3. GHSV = 7.5×10^5 h^{-1}, T_{feed} = 200 °C)

	C/O = 0.73		C/O = 1.0		C/O = 1.3	
	S/C = 0	S/C = 1	S/C = 0	S/C = 1	S/C = 0	S/C = 1
T_{back} (°C)	1082	1078	1013	999	933	922
X_{CH_4} (%)	54	56	36	33	25	27
S_{H,H_2} (%)	41	53	28	35	23	36
$S_{C,CO}$ (%)	79	76	76	70	76	70
S_{C,CO_2} (%)	16	22	16	29	20	36

Table 3
Effect of sulfur on steam addition (Catalyst Rh(0.5%)–Ce(2%), 3% γ-Al_2O_3 on 80 ppi α-Al_2O_3. GHSV = 2×10^5 h^{-1}, S/C = 2, T_{feed} = 950 °C)

Catalyst	0 ppm CH_3SH Rh–Ce	106 ppm CH_3SH Rh–Ce	Blank
T_{back} (°C)	720	925	930
X_{CH_4} (%)	34	0	0
S_{H,H_2} (%)	184	0	0

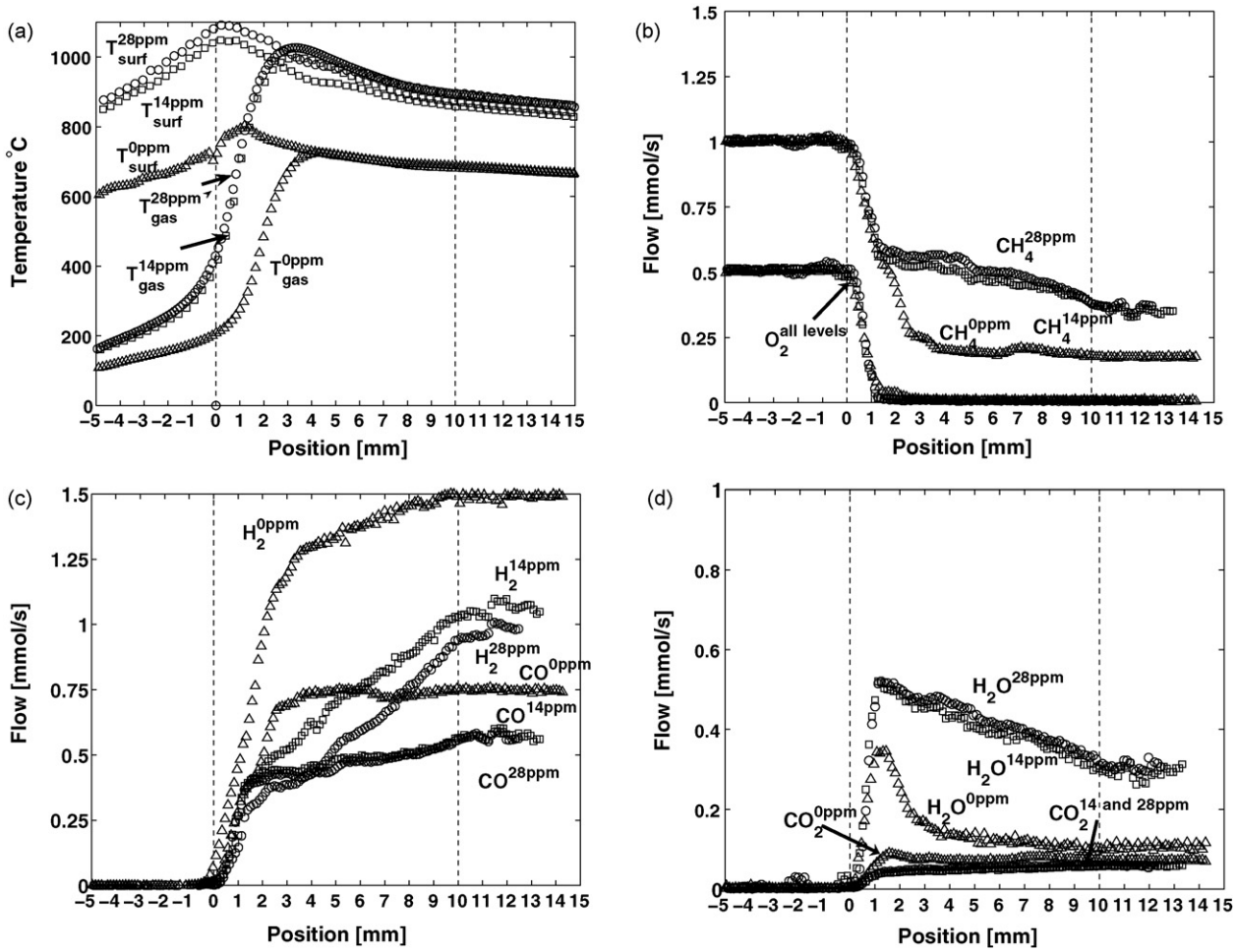

Fig. 3. Spatial profile with different levels of sulfur. Catalyst 0.5%Rh–2%Ce with 3% γ-Al_2O_3 on 80 ppi α-Al_2O_3 support. GHSV 1.4×10^5 h^{-1}. C/O = 1. (△) 0 ppm, (□) 14 ppm, and (○) 28 ppm CH_3SH, respectively. T_{feed} = 70 °C. Note only every fifth data point is plotted.

Table 4
Conversions and selectivities at 10 mm obtained in the spatial profile presented in Fig. 3 (See caption of said figure for experimental conditions)

	0 ppm	14 ppm S	28 ppm S
X_{CH_4} (%)	83	68	65
X_{O_2} (%)	100	100	100
S_{H,H_2} (%)	89	79	76
$S_{C,CO}$ (%)	91	90	88
S_{C,CO_2} (%)	9	9	9
S_{H,H_2O} (%)	12	22	24

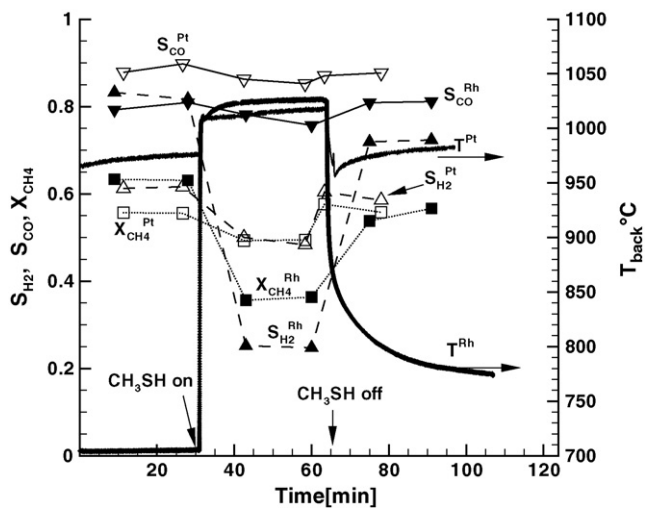

Fig. 4. Back face temperature, X_{CH_4} (□), $S_{C,CO}$(▽), and S_{H,H_2} (△) in absence and presence of 28 ppm CH_3SH. Catalyst 0.5%Rh–2%Ce (filled symbols), 0.5%Pt (open symbols) both with 3% γ-Al_2O_3 on 80 ppi α-Al_2O_3 support. GHSV 7.5×10^5 h^{-1}. C/O = 1. $T_{feed} = 200\,°C$.

28 ppm) in a feed at C/O = 1. Table 4 shows the final conversion and selectivities for the spatial profiles. It is seen that T_{surf} (pyrometer reading) and T_{gas} (thermocouple) rises by ~250° C upon the addition of 14 ppm S, and doubling this amount only leads to a further increase in the temperatures of 50 °C. The rates of O_2 conversion and the initial CH_4 conversion are independent of the sulfur level. The profiles show that the addition of sulfur not only changes the composition of the products but also changes the length of the active zone in the catalyst from ~3 mm with no sulfur to 10 mm with the addition of sulfur. Further, it is seen that H_2 and CO production decrease by about 30 and 20%, respectively. The addition of sulfur increases the amount of water significantly. This could be the result of promoted reaction paths for water formation or blocking water consuming paths. CO_2 formation is also seen to be slower either as a result of reduced WGS activity or an effect of the higher temperature which favors CO formation.

To gain further insight into the sulfur poisoning mechanism an experiment using a Pt catalyst was performed. Fig. 4 shows the effect on the introduction of 28 ppm of CH_3SH in the feed at C/O = 1 without steam. It is seen that the temperature increase is much smaller for Pt than Rh–Ce. It is also seen that while the initial conversion of CH_4 and S_{H,H_2} is lower on Pt than Rh–Ce; Pt maintains a significantly higher activity in the presence of sulfur.

4. Discussion

While sulfur is introduced in the form of CH_3SH the work by Rufael et al. showed that it dissociatively adsorbs on Pt(1 1 1) and is fully dissociated at temperatures below 300 °C [15]. It is therefore assumed that atomic sulfur is on the surface, which is corroborated by the experiments by Fisher et al. [14] that showed all sulfur is converted to H_2S and DFT calculations that show H_2S is readily dissociated on Rh [16]. The lack of sulfides is confirmed by XPS and XRD which failed to identify any formation of Rh_2S_3. It is of course possible that the amounts formed are below the detection limit. However, using the Ellingham diagrams compiled by Shatynski the ratio of H_2S/H_2 in the temperature region of interest (800–1200 °C) show that the level of sulfur would have to be much higher to form sulfides [17]. Therefore, no Rh bulk sulfides are predicted.

As is evident from Fig. 2, the introduction of even small amounts of sulfur in the feed have a dramatic effect on the performance of the catalyst. S_{H,H_2} drops from 87% to 66% while X_{CH_4} declines from 82 to 60% at C/O = 1. $S_{C,CO}$ and $S_{C,CO2}$ remains almost constant. T_{surf} and T_{gas} increase by ~200 °C. An explanation for this phenomenon is poisioning of the active catalytic sites for SR. The absence of this highly endothermic reaction would explain the temperature increase even though X_{CH_4} drops. It should also be noted that X_{O_2} (not shown) remains constant at 100% upon addition of sulfur. The absence of SR upon introduction of sulfur is further corroborated by the SR experiments where Table 3 shows complete absence of SR in the presence of sulfur. It furthermore explains the almost constant $S_{C,CO}$, since SR produces one CO for each CH_4-molecule, and the selectivity is thus not affected.

The results are in agreement with the findings of Shekhawat et al. [7] on tetradecane reforming where the detrimental effect was suggested to be due to prolonged time of organosulfur compounds on the active Rh sites or due to excessive formation of carbon on the surface. It is believed that excess carbon formation is not the cause in this work since carbon formation in CPO of CH_4 on noble metals has been shown to be very low [18]. The rapid response upon the introduction of sulfur suggests that direct poisoning of the active sites for SR is the main pathway responsible for the adverse effects of sulfur. However, sulfur poisoning is reversible as the catalyst slowly regains its activity when sulfur is removed from the feed. These results are in agreement with the results of density functional theory (DFT) calculations on Rh(2 1 1) which showed that the reactions $S + H \rightarrow SH$ and $SH + H \rightarrow H_2S$ were slow but still possible [16]. This corresponds well with our observation of slow recovery of the catalyst when sulfur is removed from the feed. Furthermore an increase in the temperature by decreasing C/O should decrease the recovery time, which is in agreement with our observations. While the recovery and observations regarding X_{CH_4}, S_{H,H_2} and $S_{C,CO}$ are in agreement with Choudhary et al., the constant conversion of O_2 upon

introduction of sulfur is not [8]. One explanation for this deviation from the reported results could be different levels of sulfur in which they used 7400 ppm of thiophene, over 250 times the amount used in the present study. It is possible that such high levels completely covers the surface and does not allow for oxygen to stick to the surface.

As shown in Table 1, the effect of sulfur is more pronounced at higher C/O-ratios with respect to loss of S_{H,H_2}. It is also noted that the temperature rise is similar for all ratios. However, the absolute temperature is not the same and that is perhaps why higher C/O-ratios (lower temperature) are affected more by S.

Steam addition to the feed (Table 1) does not change X_{CH_4}, but it does increase S_{H,H_2} and decrease $S_{C,CO}$ slightly. The effect of steam addition is virtually independent of C/O and does not appear to help keep the surface clean from sulfur.

The insight provided by the spatial profiles sheds further light on the poisoning effect of sulfur. The extreme temperature increase in the surface temperature clearly indicates that either more exothermic chemistry is going on and/or there is less endothermic chemistry in the form of SR. Inspection of the H_2O profile in Fig. 3 gives a strong indication that the temperature rise is solely due to a severe inhibition of SR. This is further supported by Fig. 2 where it is seen that the change upon introduction/removal of CH_3SH on the H_2/CH_4-ratio is three as one would expect from SR. However, sulfur does not shut down SR completely as evidenced by the continuous rise in CO and H_2 flow over the entire length of the catalyst. The extended reaction zone is ascribed to the higher operating temperature resulting from the presence of sulfur. It thus indicates that sulfur does not fully cover the surface which is in agreement with previous experiments on Rh(1 0 0) which showed that the surface saturated by 0.55 monolayers of H_2S [19].

It is also interesting that on fresh catalyst H_2 is seen earlier in the catalyst than CO, possibly due to the higher diffusion coefficient of H_2 that allows back diffusion. In the presence of sulfur this order is reversed and this must mean that CO is formed before H_2, indicating that at least some H_2 is produced by SR even in the presence of O_2.

In the literature several plausible sulfur poisoning mechanisms are proposed. They can be grouped by a purely steric effect and long-range effect. The steric effect assumes that one sulfur atom poisons one active site. The long-range effect assumes that one sulfur atom poisons multiple sites. This can occur either through changes in the electronic structure of the surrounding surface atoms or if the reaction requires an ensemble (multiple sites) by poisoning one of the sites on the ensemble [20]. The current experiments were carried out at higher temperatures than other studies, and the distinction between ensembles and pure electronic effects probably does not apply due to increased surface mobility. Furthermore Goodman's measurement of CO methanation (reverse SR) on Rh(1 1 1) showed that coverages below 0.1 monolayer of sulfur reduces catalytic activity by 80% at 327 °C. It was also shown that additional sulfur coverage only caused a small reduction of the activity. We therefore propose that the main effect of sulfur is to limit the mobility of surface species like, H(s), O(s) and OH(s) due to repulsive interactions. This interpretation is corroborated by the qualitative similarities of the spatial profiles with sulfur in the feed and previously published profiles on Pt [21]. The main difference between Rh and Pt in CPO is the difference in the higher stability of OH(s) on Pt [3]. The interpretation is also consistent with the results shown in Fig. 4 where Pt is much less affected by sulfur poisoning than Rh–Ce. The reason that the two catalysts do not become identical is due to the better sulfur tolerance of Pt than other noble metals [22]. It therefore seem likely that the effect of sulfur is to stabilize OH(s) on Rh by limiting the diffusion of either/both H(s) and O(s) and thus producing more H_2O.

5. Conclusions

The presence of small amounts of sulfur has a negative impact on the catalytic partial oxidation of methane on Rh–Ce catalysts. The CH_4 conversion and selectivity to H_2 decrease along with a sharp increase in the operating temperature. This observation was explained by sulfur poisoning of the active sites for steam reforming, probably by limiting the surface diffusion of H(s) and/or O(s). Additionally, the poisoning effect was found to be almost independent of the sulfur level over a factor of 2. The effect of sulfur results in a higher drop of S_{H,H_2} at higher C/O due to the initial lower operating temperature, which means that SR is slower. It was also found that steam in the feed did not significantly help reduce sulfur poisoning. However, regeneration of the catalyst was possible by reduction in hydrogen or a decrease in the C/O which allowed for sulfur burn off. Finally it was shown that Pt showed greater tolerance to sulfur poisoning.

Acknowledgments

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